

CONDENSATION OF ANHYDRIDES OF DICARBOXYLIC ACIDS
WITH COMPOUNDS CONTAINING ACTIVE METHYLENE GROUPS.
XIX. CONDENSATION OF PHTHALIC AND SUBSTITUTED
PHTHALIC ANHYDRIDES WITH BENZOYLACETIC ESTER

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16. Abstract Phthalylbenzoylacetic ester and its nitro and halogen derivatives were prepared through condensation of phthalic anhydride, nitrophthalic anhydride, and phthalic halide anhydride with benzoylacetic ester in a solution of acetic anhydride and triethylamine. The condensation of hemipinic acid anhydride proceeds similarly, but under more drastic conditions. Derivatives of indan-1,3-dione are also formed, with a small yield, in the reaction of nitrophthalic anhydrides with benzoylacetic ester in the presence of increased quantities of triethylamine. *PHTHALIC ANHYDRIDES WITH BENZOYLACETIC ESTER					
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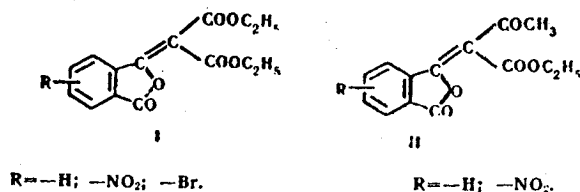
XIX. CONDENSATION OF PHTHALIC AND SUBSTITUTED
PHTHALIC ANHYDRIDES WITH BENZOYLACETIC ESTER

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Phthalylbenzoylacetic ester and its nitro and halogen derivatives/420* were produced through condensation of phthalic anhydride, nitrophthalic anhydride, and phthalic halide anhydride with benzoylacetic ester in a solution of acetic anhydride and triethylamine. The condensation of hemipinic acid anhydride proceeds similarly, but under more drastic conditions. Derivatives of indan-1,3-dione are also formed, with a small yield, in the reaction of nitrophthalic anhydrides with benzoylacetic ester in the presence of increased quantities of triethylamine.

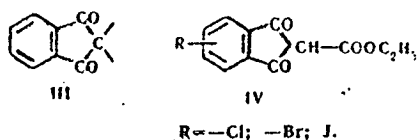
Phthalic anhydride, in a solution of acetic anhydride in the presence of triethylamine, at room temperature easily condenses with esters containing active methylene groups [1]. Interaction with malonic ester forms a product of crotonic condensation of the carbonyl group of the cyclic anhydride -- phthalylmalonic ester (I; R = H).



Also described are reactions of 3-nitro- [2], 4-nitro- [3], and 3-bromophthalic [4] anhydrides with malonic ester, leading to the substitution in the benzene ring of a phthalylmalonic ester derivative (I; R = -NO₂, -Br). Acetoacetic ester, on the other hand, in a reaction with phthalic anhydride yields both a product of the condensation of the active methylene group with the anhydride's carbonyl oxygen (II;

*Numbers in the margin indicate pagination in the foreign text.

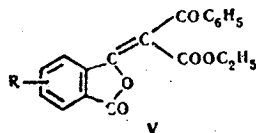
R = H) and a product in which the anhydride oxygen is replaced by a carbon of the methylene component (III). The direction of the reaction depends on the amount of triethylamine used in the reaction [1].



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While the behavior of nitrophthalic anhydrides is analogous to the above [2, 3], with condensation of halogen-substituted phthalic anhydrides with acetoacetic ester it has so far proven possible to produce only products with an indan dione structure (IV) [5], from which it is easy to obtain the corresponding indan-1,3-dione halides with a free methylene group.

By structure, benzoylacetic ester is close to acetoacetic ester, so it was of interest to study its behavior in reactions with cyclic anhydrides of dicarboxylic acids. It turned out that benzoylacetic ester easily condenses with phthalic anhydride at room temperature, and also with nitrophthalic anhydride and phthalic halide anhydrides, in a solution of acetic anhydride and triethylamine. The obtained compounds represent white crystalline substances whose elemental composition and IR spectroscopy data (Table 1) demonstrate their belonging to the 3-methylene phthalide series (V).



R = -H; -NO₂; -Cl; Br; -J.

When the concentration of triethylamine in the reaction solution is increased, phthalylbenzoylacetic ester (V; R = H) remains virtually the sole product of the condensation of unsubstituted phthalic anhydride with benzoylacetic ester. Condensation of nitrophthalic anhydrides with benzoylacetic ester in the presence of increased quantities of triethylamine produces products of phthalide structure (V; R = -NO₂) that crystallize out of the reaction solution, but it also produces compounds having the structure of derivatives of indan-1,3-dione (III) that remain in solution. They could not be isolated in pure form, but


VIa

Experimental Part

1.48 g (0.01 mole) of phthalic anhydride and 1.92 g (0.01 mole) of benzoylacetic ester, under moderate heating, are dissolved in 5 g (0.05 mole) of acetic anhydride and 1 g (0.01 mole) of triethylamine is added at room temperature. The reaction mixture is left in a covered flask for 24 hours, after which 20 g of ice and 5 ml of concentrated hydrochloric acid are poured into the mixture. The precipitate forming after a period of time is filtered out and dried. The weight is 2.8 g (86.9%), the melting point 85-90°. After triple crystallization from ethanol the melting point is 110-111°. For elemental analysis data, see the table.

PRODUCTS OF THE CONDENSATION OF PHTHALIC AND SUBSTITUTED
PHTHALIC ANHYDRIDES WITH BENZOYLACETIC ESTER

No.	Obtained product	Melt- ing point, °C	General formula	Element analysis			
				Discovered, %			
				C	H	N	halo- gen
1	Phthalylbenzoylacetic ester	110—111	C ₁₉ H ₁₄ O ₅	70,52	4,26	—	—
2	4- (or 7-)Nitrophthalylbenzoylacetic ester	229—230	C ₁₉ H ₁₃ O ₇ N	62,52	3,50	3,98	—
3	5- (or 6-)Nitrophthalylbenzoylacetic ester	200—201	C ₁₉ H ₁₃ O ₇ N	62,22	3,55	3,67	—
4	4- (or 7-)Chlorophthalylbenzoylacetic ester	179—180	C ₁₉ H ₁₃ O ₅ Cl	64,09	3,74	—	9,62
5	5- (or 6-)Chlorophthalylbenzoylacetic ester	166—167	C ₁₉ H ₁₃ O ₅ Cl	64,32	3,74	—	9,91
6	4- (or 7-)Bromophthalylbenzoylacetic ester	185—187	C ₁₉ H ₁₃ O ₅ Br	56,85	3,51	—	19,57
7	5- (or 6-)Bromophthalylbenzoylacetic ester	153—155	C ₁₉ H ₁₃ O ₅ Br	57,00	3,55	—	20,16
8	5- (or 6-)Iodophthalylbenzoylacetic ester	172—173	C ₁₉ H ₁₃ O ₅ I	51,18	2,70	—	28,06
9	4,5- (or 6,7-)Dimethoxyphthalylbenzoylacetic ester	174—175	C ₂₁ H ₁₈ O ₇	66,16	4,95	—	—

No.	Element analysis				IR spectroscopy*			
	calculated, %				stretch vibration frequencies, cm ⁻¹			
	C	H	N	halo- o- gen	$\nu_{\text{C=O}}$ phthal- ide ring	$\nu_{\text{C=O}}$ ketone or ester	$\nu_{\text{C=C}}$ or aromatic	ν_{NO_2}
1	70,80	4,38	—	—	1797 (78)	1717 (66); 1679(72)	1638(76); 1599(46)	—
2	62,13	3,57	3,81	—	1812(83)	1724(85); 1668(82)	1623(68); 1599(47); 1582(45)	1540(78)
3	62,13	3,57	3,81	—	1816(84)	1712(77); 1673(81)	1644(79); 1599(64); 1583(48)	1537(80)
4	63,97	3,67	—	9,94	1792(62)	1718(57); 1670(61)	1629(64); 1594(57); 1583(58)	—
5	63,97	3,67	—	9,94	1803(72)	1711(61); 1677(65)	1633(67); 1597(56); 1579(52)	—
6	56,88	3,27	—	19,92	1788(75)	1719(72); 1673(72)	1635(76); 1592(66); 1576(63)	—
7	56,88	3,27	—	19,92	1801(83)	1710(72); 1677(76)	1632(79); 1600(64); 1578(55)	—
8	50,92	2,92	—	28,31	1812(79)	1704(62); 1677(81)	1629(76); 1596(53); 1574(37)	—
9	65,97	4,74	—	—	1789(88)	1722(89); 1665(82)	1632(84); 1598(76)	—

*For solids in paraffin oil, taken in IKS-14 instrument.

Condensation of substituted phthalic anhydrides with benzoylacetic ester. 0.01 mole of 3- or 4-nitro-, 3- or 4-chloro-, 3- or 4-bromo-, or 4-iodophthalic anhydride is condensed with 1.92 g (0.01 mole) of benzoylacetic ester in a solution of 5 g (0.05 mole) of acetic anhydride and 1 g (0.01 mole) of triethylamine, as described above. Falling out of the reaction solution is a white precipitate that is filtered out, washed with a small amount of acetic acid, and dried. The yield is 40-75%. It is crystallized from glacial acetic acid for purification. The melting point and analysis data are cited in the table.

Condensation of nitrophthalic anhydrides with benzoylacetic ester in the presence of increased quantities of triethylamine. 3- or 4-nitrophthalic anhydride is condensed with benzoylacetic ester using the procedure presented above, the only difference being that 3 g (0.03 mole) of triethylamine is used. The precipitate is filtered out, and after crystallization it turns out to be identical to that obtained above. The filtrate is poured into a mixture of 20 g ice and 5 ml concentrated hydrochloric acid. The precipitate thus formed is isolated and dried. /423

Obtained from the product of 3-nitrophthalic anhydride is 1.05 g of a substance that after boiling with 100 ml of water and 5 ml of concentrated hydrochloric acid, using the procedure in [2], yields 0.32 g 4-nitroindan-1,3-dione with a melting point of 132° (in [2] the melting point is 133-135°).

Discovered %: N 7.40. $C_9H_5O_4N$. Calculated %: N 7.33.

The condensation product of 4-nitrophthalic anhydride produces 1.9 g of a substance that after similar treatment yields a small amount of 5-nitroindan-1,3-dione.

Discovered %: N 7.49. $C_9H_5O_4N$. Calculated %: N 7.33.

Condensation of hemipinic acid anhydride with benzoylacetic ester. 2.08 g (0.01 mole) of hemipinic acid anhydride and 1.92 g (0.01 mole) of benzoylacetic ester are dissolved in a heated water bath in 5l g

(0.5 mole) of acetic anhydride and 6.1 g (0.06 mole) of triethylamine is added. Heating in a water bath is conducted for 30 min, after which the solution is poured into 200 g of ice and 50 ml of concentrated hydrochloric acid. After filtration and drying, 1.8 g (47.1%) of material is obtained which after double crystallization from acetic anhydride melts at 174-175° (table).

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